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71 Applicant: **DOWELL SCHLUMBERGER  
INCORPORATED  
P.O.Box 4378  
Houston Texas 77210(US)**

72 Inventor: **Frenier, Wayne W.  
7514 S. 68th East Place  
Tulsa, OK 74133(US)  
Inventor: Growcock, Frederick B.  
8308 Broken Arrow  
OK 74011(US)**

74 Representative: **Richebourg, Michel François  
Etudes et Fabrication Dowell Schlumberger  
Z.I. Molina La Chazotte B.P. 90  
F-42003 Saint-Etienne Cédex 1(FR)**

54 **Process and composition for inhibiting iron and steel corrosion.**

57 **A composition and method for inhibiting the attack of aqueous corrosive fluids on metal by contacting the metal with a composition including an  $\alpha,\beta$ -unsaturated aldehyde and a surfactant.**

**EP 0 289 665 A1**

## PROCESS AND COMPOSITION FOR INHIBITING IRON AND STEEL CORROSION

### BACKGROUND OF THE INVENTION

#### 5 Field of the Invention

This invention relates to novel corrosion inhibiting compositions and to processes of using them. More particularly, this invention relates to novel corrosion-inhibiting compositions which reduce the attack of  
10 various aqueous fluids, including aqueous acids, alkaline solutions and heavy brines, on ferrous metals, such as iron and steel, and to processes of using such compositions.

#### Description of the Prior Art

15

Aqueous acids, alkaline solutions and heavy brines are known to damage ferrous metal surfaces. These corrosive substances are often found in or added to crude oils and intermediate or final products made therefrom. In addition, when exploring for and recovering petroleum from underground fields it is common  
20 to "acidize" new and producing wells with aqueous solutions of strong acids. This of course can lead to corrosion of well casings, pumps and other ferrous metal-containing equipment.

Similarly, acidic materials are often generated in equipment used in processing or transporting petroleum refinery streams, where water vapor can combine with acidic gases evolved during refinery operations to yield corrosive gases.

25 Various materials for inhibiting the attack of corrosive fluids on ferrous metals are known, but few provide satisfactory protection. Arsenic and various arsenic compounds, for example, have been used, notwithstanding their toxicity, as acid corrosion inhibitors for ferrous metals. However, the adverse effect arsenic and arsenic compounds have on catalysts used in petroleum refineries, coupled with their toxicity, has lead the industry to search for corrosion inhibitors which are free of such undesirable properties.

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#### Aldehyde-Containing Corrosion-Inhibitors

35 U.S. Patent No. 3,077,454, issued February 12, 1963 to Monroe et al and assigned to The Dow Chemical Company, discloses inhibitors of aqueous acid attack on metals which comprise certain active nitrogen-containing compounds, e.g., primary and secondary amines, admixed with ketones and aliphatic or aromatic aldehydes.

Three patents issued to Foroulis and assigned to Esso Research and Engineering Company, U.S.  
40 Patent No. 3,530,059, issued September 22, 1970, U.S. Patent No. 3,537,974, issued November 3, 1970 and U.S. Patent No. 3,589,860, issued June 29, 1971, all disclose the use of aldehydes to prevent corrosion of metals such as steel by aqueous acidic solutions. Alkyl aldehydes in which the aldehyde group is attached to the aliphatic side chain are the corrosion-preventing aldehydes disclosed in the first of these patents. The second Foroulis patent discloses alkoxy-substituted benzaldehydes, such as p-methoxybenzal-  
45 dehyde, as corrosion inhibitors, while the third Foroulis patent discloses the use of cinnamic aldehyde (i.e., cinnamaldehyde) and certain derivatives thereof for this purpose.

U.S. Patent No. 3,854,959 issued December 17, 1974 to Costain et al and assigned to ICI, discloses mixtures of a nitrile or an oxime with aldehydes as corrosion inhibitors for steel.

A paper by Hugel entitled "Corrosion Inhibitors; Study of Their Active Mechanism", delivered at the  
50 Tenth Meeting of the European Corrosion Federation, Ferrara, Italy, September 28-October 1, 1960, discloses that a number of aldehydes have been tested for corrosion inhibition (see, for example, Table I).

A paper by Derarajan et al entitled "Aldehydes as Inhibitors of Corrosion of Mild Steel in Acids", Trans. SAEST, 19, 1, 71-81 (1984) states (at page 75) that "(i)n acid solutions cinnamaldehyde is found to exhibit the highest efficiency in reducing corrosion."

A paper by Rocchini entitles "A Study of the Acid Cleaning of a Steam Generator Performed with a Pilot Plant - Part I" delivered at CORROSION '85, Boston, Massachusetts March 25-29, 1985, discloses at page 188/7 that a commercial inhibitor, BORG p 16, is derived from Rodine 213, with the addition of cinnaminaldehyde to improve its thermal stability.

5

#### Surfactant-Containing Corrosion-Inhibitors

10 Fedorov et al, Zasch. Metal., 1971, 7(1), 73-6, CA 74, 82362J, discloses that certain organic thiocyanates and indole derivatives which behave as surface active agents have a corrosion inhibiting effect on steel in acid solution.

U.S. Patent No. 4,493,775, issued January 15, 1985 to Coffey et al and assigned to The Dow Chemical Company, discloses corrosion-inhibiting formulations in which formaldehyde is both a reactant and an unreacted constituent (present in excess). These formulations may, but need not, also contain a surfactant.

15 Pending U.S. patent application Serial No. 06/765,890, filed August 14, 1985, by W. Frenier, V.R. Lopp, F. Growcock and B. Dixon, discloses and claims inhibiting corrosion of iron and steel in contact with aqueous acids by using compositions which contain an alkenylphenone derivative and which may contain, but need not contain, a surfactant as well.

20

#### SUMMARY OF THE INVENTION

25 It has now been discovered that certain aldehydes, in combination with a surfactant, provide corrosion-inhibiting compositions which reduce the attack of various aqueous fluids, such as aqueous acids, alkaline solutions and heavy brines, on ferrous metals, such as iron and steel, as well as on non-ferrous metals, such as aluminum, zinc and copper. Surprisingly, such aldehyde and surfactant containing corrosion-inhibiting compositions provide greater and more reliable corrosion inhibition than do compositions contain-  
30 ing the aldehydes alone.

It is, therefore, an object of this invention to provide improved compositions for inhibiting metal corrosion caused by corrosive aqueous fluids.

Another object of the invention is to provide improved compositions for inhibiting ferrous metal corrosion caused by corrosive aqueous fluids, which corrosion-inhibiting compositions comprise certain  
35 aldehydes and a surfactant.

It is also an object of this invention to provide an improved method of inhibiting ferrous metal corrosion caused by corrosive aqueous fluids.

A further object of the invention is to provide an improved method of inhibiting ferrous metal corrosion caused by aqueous fluids which comprises mixing certain aldehydes and a surfactant together with such  
40 corrosive aqueous fluids.

These and other objects, as well as the nature, scope and utilization of the invention, will become readily apparent to those skilled in the art from the following description and the appended claims.

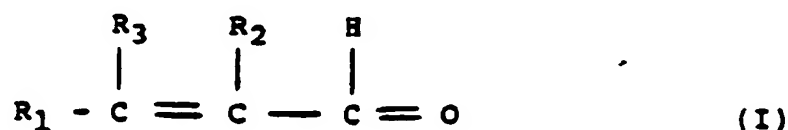
#### DETAILED DESCRIPTION OF THE INVENTION

##### The Aldehydes

50

The aldehydes used in the novel corrosion-inhibiting compositions of the present invention are  $\alpha$ ,  $\beta$  - unsaturated aldehydes having the general formula:

55



wherein:

R<sub>1</sub> represents a saturated or unsaturated aliphatic hydrocarbon group containing from about 3 to about 12 carbon atoms, a substituted saturated or unsaturated aliphatic hydrocarbon group containing from about 3 to about 12 carbon atoms and also containing one or more non-interfering substituents, an aryl group, e.g., phenyl, benzyl or the like, a substituted aryl group containing one or more non-interfering substituents, or a non-interfering substituent per se.

R<sub>2</sub> represents hydrogen, a saturated or unsaturated aliphatic hydrocarbon group containing from 1 to about 5 carbon atoms, a substituted saturated aliphatic hydrocarbon group containing from 1 to about 5 carbon atoms and also containing one or more non-interfering substituents, an aryl group, a substituted aryl group containing one or more non-interfering substituents, or a non-interfering substituent per se, and

R<sub>3</sub> represents hydrogen, a saturated or unsaturated aliphatic hydrocarbon group containing from about 3 to about 12 carbon atoms, a substituted saturated or unsaturated aliphatic hydrocarbon group containing from about 3 to about 12 carbon atoms and also containing one or more non-interfering substituents, an aryl group, a substituted aryl group containing one or more non-interfering substituents, or a non-interfering substituent per se, with the total number of carbon atoms in substituents represented by R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> ranging from 1 to about 16, and preferably from about 5 to about 10.

Non-interfering substituents referred to above which replace hydrogen on the  $\alpha$ - and  $\beta$ -carbon atoms of the aldehydes of formula I above or which are found in hydrocarbon substituents which replace hydrogen on these carbon atoms and have no adverse effect on the corrosion inhibition are provided by the novel compositions of this invention. They include, for example, lower alkyl (containing from 1 to about 4 carbon atoms), lower alkoxy (containing from 1 to about 4 carbon atoms), halo, i.e., fluoro, chloro, bromo or iodo, hydroxyl, dialkylamino, cyano, thiocyno, N,N-dialkylcarbamoylthio and nitro substituents.

Included among the  $\alpha$ ,  $\beta$ -unsaturated aldehydes represented by formula I above are crotonaldehyde,

2-hexenal,

2-heptenal,

2-octenal,

2-nonenal,

2-decenal,

2-undecenal,

2-dodecenal,

2,4-hexadienal,

2,4-heptadienal,

2,4-octadienal,

2,4-nonadienal,

2,4-decadienal,

2,4-undecadienal,

2,6-dodecadienal,

citral,

1-formyl-[2-(2-methylvinyl)]-2-n-octylethylene,

cinnamaldehyde,

dicinnamaldehyde,

p-hydroxycinnamaldehyde,

p-methylcinnamaldehyde,

p-ethylcinnamaldehyde,

p-methoxycinnamaldehyde,

p-dimethylaminocinnamaldehyde,

p-diethylaminocinnamaldehyde,

p-nitrocinnamaldehyde,

o-nitrocinnamaldehyde,

o-allyloxycinnamaldehyde,

4-(3-propenal)cinnamaldehyde,

p-sodium sulfocinnamaldehyde,

p-trimethylammoniumcinnamaldehyde sulfate,

p-trimethylammoniumcinnamaldehyde o-methylsulfate,

p-thiocyanocinnamaldehyde,

p-(S-acetyl)thiocinnamaldehyde,

p-(S-N,N-dimethylcarbamoylthio)cinnamaldehyde,

p-chlorocinnamaldehyde,  
 5-phenyl-2,4-pentadienal,  
 5-(p-methoxyphenyl)-2,4-pentadienal,  
 2,3-diphenylacrolein,  
 5 3,3-diphenylacrolein,  
 α-methylcinnamaldehyde,  
 β-methylcinnamaldehyde,  
 α-chlorocinnamaldehyde,  
 α-bromocinnamaldehyde,  
 10 α-butylcinnamaldehyde,  
 α-amylicinnamaldehyde,  
 α-hexylcinnamaldehyde,  
 2-(p-methylbenzylidene)decanal,  
 α-bromo-p-cyanocinnamaldehyde,  
 15 α-ethyl-p-methylcinnamaldehyde,  
 p-methyl-α-pentylcinnamaldehyde,  
 3,4-dimethoxy-α-methylcinnamaldehyde,  
 α-[(4-methylphenyl)methylene] benzeneacetaldehyde,  
 α-(hydroxymethylene)-4-methylbenzylacetaldehyde,  
 20 4-chloro-α-(hydroxymethylene) benzeneacetaldehyde,  
 α-nonylidenebenzeneacetaldehyde,  
 and the like, preferably in their trans forms. Transcinnamaldehyde is a preferred aldehyde for use in practicing this invention.

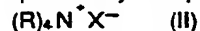
From about 0.01 to about 4 percent by weight, and preferably from about 0.05 to about 1 percent by weight, of one or a mixture of the aldehydes of formula I above, based on the total weight of (1) aldehyde, (2) surfactant and (3) the aqueous fluid being treated, will be employed together with surfactant to inhibit ferrous metal corrosion.

### 30 The Surfactants

Anionic, cationic, nonionic and amphoteric surfactants can be used together with the α,β -unsaturated aldehydes of formula I above in the novel corrosion-inhibiting compositions of this invention.

35 Anionic surfactants useful in these compositions include alkyl sulfates, such as the sodium alkyl sulfates prepared by the sulfation of higher alcohols derived from coconut oil or tallow fatty alcohols, alkyl aryl sulfonates, such as polypropylene benzene sulfonates, dialkyl sodium sulfosuccinates such as dioctyl sodium sulfosuccinate,  
 40 and the like.

Cationic surfactants which can be used in these compositions include nitrogen atom-containing quaternary compounds of the general formula



45 wherein the R's represent the same or different longchain alkyl, cycloalkyl, aryl or heterocyclic groups, and X represents an anion, usually a halide or methosulfate. Among such quaternary compounds are N-alkyl, N-cycloalkyl and N-alkylaryl pyridinium halides such as

N-cyclohexylpyridinium bromide  
 N-octylpyridinium bromide,  
 N-nonylpyridinium bromide,  
 50 N-decylpyridinium bromide,  
 N-dodecylpyridinium bromide,  
 N,N-dodecylpyridinium dibromide,  
 N-tetradecylpyridinium bromide,  
 N-laurylpyridinium chloride,  
 55 N-dodecylbenzylpyridinium chloride,  
 N-dodecylquinolinium bromide quinolinium-(1-naphylenemethyl) chloride  
 and the like.

Other quaternary ammonium compounds include monochloromethylated and bischloromethylated

pyridinium halides, ethoxylated and propoxylated quaternary ammonium compounds, sulfated ethoxylates of alkyl phenols and primary and secondary fatty alcohols, didodecyldimethylammonium chloride, hexadecylethyltrimethylammonium chloride,

- 5 2-hydroxy-3-(2-undecylamidoethylamino)-propane-1-triethylammonium hydroxide,  
2-hydroxy-3-(2-heptadecylamidoethylamino)-propane-1-triethylammonium hydroxide,  
2-hydroxy-3-(2-heptadecylamidoethylamino)-propane-1-triethylammonium hydroxide,  
and the like.

The cationic surfactants which can be used also include covalently-bonded nitrogen compounds such as primary amines, secondary amines, or tertiary amines, e.g. dodecyl dimethyl amine.

10 Nonionic surfactants which can be used in the corrosion-inhibiting compositions of this invention include ethoxylates of alkyl phenols, primary fatty alcohols, secondary fatty alcohols, and the like, including alkyl and alkylaryl polyether alcohols such as the reaction product of trimethyl-1-heptanol with seven mols of ethylene oxide, the reaction products of octyl or nonyl phenol with, e.g., from about 8 to 30 mols or more of  
15 ethylene oxide, polyoxyethylenepolyoxypropylene block copolymers, and the like.

Amphoteric surfactants useful in practicing this invention include coco- $\beta$ -aminopropionate and the like.

From about 0.005 to about 1 percent by weight, and preferably from about 0.01 to about 0.5 percent by weight, of surfactant, based on the total weight of (1) aldehyde, (2) surfactant and (3) the aqueous fluid being treated, will be employed, together with one or more aldehydes of formula I above, to inhibit ferrous metal corrosion.

Among the corrosive aqueous fluids to which the novel compositions of this invention may be added to inhibit corrosion of ferrous metals such as iron and steel, e.g., oil field goods, mild steel, refinery equipment, etc., in contact with such fluids are:

(1) Aqueous solutions of non-oxidizing mineral or organic acids, for example hydrochloric acid, hydrofluoric acid, sulfuric acid, phosphoric acid, formic acid, acetic acid, citric acid, and mixtures thereof. Such acid solutions may also contain chelating agents, such as EDTA, HEDTA, DPTA and the like. The concentration of non-oxidizing mineral or organic acid in such aqueous solutions may vary from about 0.1 to about 35% by weight, based on the total weight of the solution, and the temperature may vary from ambient up to about 300°F. (150°C).

(2) Aqueous solutions of alkaline chelating agents, such as the ammonium salts of EDTA, HEDTA, and DPTA. The alkaline chelating agent may be present in such solutions in an amount ranging from about 0.1 to about 15% by weight, based on the total weight of the solution. The temperature of these solutions may vary from ambient up to about 300°F. (150°C).

(3) Aqueous salt solutions or brines, sometimes characterized as "heavy brines", such as solutions of sodium chloride, potassium chloride, calcium chloride, calcium bromide, zinc bromide and mixtures of such salts. Salt concentrations in such solutions may vary from about 0.1% by weight to saturation, based on the total weight of the solution. These salt solutions may be mixed with an acid gas, such as carbon dioxide or hydrogen sulfide, and with hydrocarbons such as mineral oil, crude oil and refined hydrocarbon products. The temperature of these salt solutions may vary from ambient up to about 400°F. (200°C).

The corrosion-inhibiting compositions of this invention will ordinarily be employed, in the amounts indicated above, at temperatures preferably ranging from about 20°C to about 200°C. However, the use of amounts of these corrosion-inhibiting compositions outside the above-disclosed ranges is also within the invention, and will depend on such factors as the particular corrosive liquid being treated, the water solubility of the inhibitor composition, the temperature of the corrosive liquid and its time in contact with the inhibitor composition, etc. The exact amount of inhibitor composition to employ in any particular instance can be determined using the test methods described in the examples below. These examples, which are given solely for purposes of illustration to aid those skilled in the art to more fully understand the invention, should not be considered as expressing limitations unless so set forth in the appended claims. All parts and percentages are by weight, unless otherwise stated.

#### Comparative Example 1

API grade J55 oil field steel coupons having a surface area of 25.8 cm<sup>2</sup> were cleaned and weighed. The steel coupons were cleaned in an ultrasonic cleaner containing a chlorinated hydrocarbon solvent, rinsed

with acetone, dried and weighed. Each coupon was hung from a glass hook attached to the lid of a 4-oz bottle. The coupon was immersed in 100 ml of 15% (by weight) hydrochloric acid contained in the bottle and then heated at 150°F. (66°C.) in a water bath for 24 hours. At the end of this time, the vessel was cooled, the coupons were removed, cleaned with a soft brush, dried with acetone and reweighed.

5 The uninhibited corrosion or weight loss rate is calculated from the following equation:

$$\text{weight loss rate}^a/ = \frac{w^b/ \times 49.15^c/}{t^d/ \times S.A.^e/}$$

10

a/ In lb/ft<sup>2</sup>/day.

b/ Change in weight of coupon, expressed in grams.

c/ A unit conversion factor.

d/ Testing time, expressed in hours.

15

e/ Surface area of coupon, expressed in cm<sup>2</sup>.

The uninhibited corrosion rate was found to be 1.06 lb/ft<sup>2</sup>/day. When the test was rerun once again using 200 mg of trans-cinnamaldehyde (TCA) the corrosion rate was reduced to 0.075 lb/ft<sup>2</sup>/day. The percent protection afforded by TCA alone was calculated from the following equation:

20

$$\text{Percent Protection} = \frac{(\text{Corrosion Rate without Inhibitor} - \text{Corrosion Rate with Inhibitor}) \times 100}{\text{Corrosion Rate without Inhibitor}}$$

25

Thus, TCA afforded 93% protection for J55 steel. When tested under identical conditions, phenylacetaldehyde, 2-phenylpropionaldehyde and 3-phenylpropionaldehyde afforded 0% protection to J55 steel.

The percent protection afforded by TCA alone was not, however, reproducible. The results of four identical runs as described above with TCA alone, using J55 steel coupons, at 150°F. (66°C.), 15% HCl, 24-hour tests, are set forth below.

30

<u>Inhibitor</u>	<u>[Inhibitor], g /100 ml</u>	<u>% Protection</u>
TCA	0.20	55.7
TCA	0.20	89.1
TCA	0.20	94.7
TCA	0.20	3.8

35

40

### Comparative Example 3

45

Using the general method of Comparative Example 1, surfactants were tested in 15% hydrochloric acid at 150°F. (66°C.). Three known surfactant corrosion inhibitors were tested. The three inhibitors were cyclododecylamine (200 mg/100 ml), dodecylpyridinium bromide (50 mg/100 ml), and dodecylquinolinium bromide (50 mg/100 ml).

50

The percent protection afforded by each of those inhibitors for each type of steel is given in the following table:

55

Table IPercent ProtectionInhibitorJ55 Steel

Cyclododecylamine

75%

Dodecylpyridinium bromide (DDPB)

50%

Dodecylquinolinium bromide

15%

In an indential test of DDPB at 50 mg/100 ml, conducted at another time, DOPB provided 0% protection for J55 steel.

Example I

The procedure of Comparative Example 1 was repeated eight times in every respect except for the variations shown in Table II below. Runs 1 and 5 are comparative runs, carried out without surfactant. Runs 2-4 and 6-8 demonstrate the protection afforded to steel samples in a corrosive acidic liquid by TCA in combination with surfactants.



Table II

Run No.	HCl, Weight %	Surfactant	TCA / Surfactant,		Protection
			mg/100 ml		
1	15	-	200	0	93.0
2	15	THBO <sup>1</sup>	200	50	98.0
3	15	DDPB <sup>2</sup>	200	50	99.2
4	15	POLYSTEP A18 <sup>3</sup>	200	50	98.4
5	28	-	400	0	0
6	28	THBO	400	100	81.7
7	28	DDPB	400	100	98.2
8	28	POLYSTEP A18	400	100	99.1

0 289 665

1. Trimethyl-1-heptanol reacted with 7 mols of ethylene oxide.
2. Dodecylpyridinium bromide.
3. A commercially available sulfonate surfactant; from Stepan Chemical Co., Northfield, IL 60093.

Example II

The procedure of Comparative Example 1 was again repeated in every respect, except for the variations shown in Table III below, to demonstrate the protection afforded to J55 steel samples in corrosive acidic liquids by aldehydes coming within the scope of formula I above in combination with surfactants.

Table III

## PERCENT PROTECTION

Run No.	Inhibitor	158 HCl		288 HCl	
		200 mg Inhibitor /50 mg DDPB		400 mg Inhibitor /100 mg DDPB	
1	Crotonaldehyde	73.8		64.8 <sup>b</sup>	
2	t-2-Hexenal	92.8		-	
3	t,t-2,4-Heptadienal	97.3		8.3 <sup>b</sup>	
4	t-2-Nonenal	94.7		-	
5	5-(p-Methoxyphenyl)- -2,4-pentadienal	94.4		-	
6	t-Cinamaldehyde	99.2		98.4	
7	p-Chlorocinnamaldehyde	99.4		0	
8	α-Bromo-p-cyanocinnam- aldehyde	75.5		-	
9	α-Ethyl-p-methylcinnam- aldehyde	95.7 <sup>a</sup>		-	
10	α-Methylcinnamaldehyde	96.7 <sup>a</sup>		-	
11	α-Amylcinnamaldehyde	93.5 <sup>a</sup>		-	
12	2,3-Diphenylacrolein	95.9 <sup>a</sup>		-	
13	α-Chlorocinnamaldehyde	98.4		97.7	
14	α-(Hydroxymethylene)-4- methylbenzeneacetaldehyde	94.2		-	
15	α-Ethyl-p-methylcinnam- aldehyde	93.5 <sup>a</sup>		-	
16	α-[(4-Methylphenyl)- methylene] benzeneacet- aldehyde	37.7 <sup>a</sup>		-	

Table III (Continued)

<u>Run No.</u>	<u>Inhibitor</u>	<u>PERCENT PROTECTION</u>	
		<u>150 HCl 200 mg Inhibitor /50 mg DOPB</u>	<u>280 HCl 400 mg Inhibitor /100 mg DOPB</u>
17	$\alpha$ -Nonylidenebenzene- acetaldehyde	91.2 <sup>a</sup>	-
18	3,3-Diphenylacrolein	84.3	7.3
19	Citral	94.4	-

a. Concentration of Inhibitor = 100 mg/100 ml

b. Surfactant is THBO.

Example III

Control Values for THEO and DDPB  
 Conditions: 66°C., 24-hr. Tests, J55 Steel

<u>Material</u>	<u>% HCl</u>	<u>[Material] g /100 ml</u>	<u>% Protection</u>
THEO	15	0.05	0
THEO	15	0.20	0
THEO	28	0.10	0
DDPB	15	0.05	0
DDPB	15	0.20	55
DDPB	28	0.10	33
DDPB	28	0.20	15

Example IV

Effect of Surfactant Concentration and  
 TCA Concentration in 28% HCl  
 J55, 66°C., 24-hr. Tests

<u>Surfactant</u>	<u>[TCA] g /100 ml</u>	<u>[Surfactant] g /100 ml</u>	<u>% Protection</u>
POLYSTEP A18	0.50	0.10	99.0
POLYSTEP A18	0.45	0.40	97.4
DDPB	0.20	0.20	4.9
DDPB	0.30	0.30	65.0
DDPB	0.40	-	0
DDPB	0.40	0.20	97.3
DDPB	0.40	0.40	95.1

Example V

## Effect of Acid Concentration &amp; Steel

4.0 hr., 29°C., [TCA] = 0.32 g /100 ml  
 [DDPB] = 0.08 g /100 ml

% HCl	% Protection		
	AISI 1008	AISI 1026	API J55
1	99.3	99.3	90.8
5	99.5	99.6	93.2
10	99.4	99.7	94.9
15	99.4	99.9	96.8
20	99.8	99.7	97.9
28	99.9	99.9	98.8

Example VI

## Effect of Steel

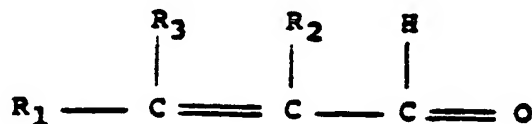
20% HCl, 3.2 hr, 200°F. (93°C.)  
 [TCA] = 0.16 g /100 ml  
 [DDPB] = 0.04 g /100 ml

Steel	% Protection
AISI 1008	99.7
AISI 1026	99.3
API J55	98.5

The above discussion and related illustrations of this invention are directed primarily to preferred embodiments and practices thereof. It will be readily apparent to those skilled in the art, however, that numerous changes and modifications in the actual implementation of the concepts described herein can readily be made without departing from the spirit and scope of the invention as defined by the following claims.

## Claims

1. A composition for inhibiting the attack of aqueous corrosive fluids on ferrous metal which comprises:  
 (A) an  $\alpha,\beta$ -unsaturated aldehyde having the general formula:



wherein:

R<sub>1</sub> represents a saturated or unsaturated aliphatic hydrocarbon group containing from about 3 to about 12 carbon atoms, a substituted saturated or unsaturated aliphatic hydrocarbon group containing from about 3 to about 12 carbon atoms and also containing one or more non-interfering substituents, an aryl group, a substituted aryl group containing one or more non-interfering substituents, or a non-interfering substituent per se.

R<sub>2</sub> represents hydrogen, a saturated or unsaturated aliphatic hydrocarbon group containing from 1 to about 5 carbon atoms, a substituted saturated or unsaturated aliphatic hydrocarbon group containing from 1 to about 5 carbon atoms and also containing one or more non-interfering substituents, an aryl group, a substituted aryl group containing one or more non-interfering substituents, or a non-interfering substituent per se, and

R<sub>3</sub> represents hydrogen, a saturated or unsaturated aliphatic hydrocarbon group containing from about 3 to about 12 carbon atoms, a substituted saturated or unsaturated aliphatic hydrocarbon group containing from about 3 to about 12 carbon atoms and also containing one or more non-interfering substituents, an aryl group, a substituted aryl group containing one or more non-interfering substituents, or a non-interfering substituent per se, with the total number of carbon atoms in substituents represented by R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> ranging from 1 to about 16, and

(B) a surfactant.

2. A composition as set forth in claim 1 wherein said aldehyde is present in an amount of from about 0.01 to about 4 percent by weight and said surfactant is present in an amount of from about 0.005 to about 1 percent by weight, said percentages being based on the total weight of said aldehyde, said surfactant and said aqueous corrosive fluid.

3. A composition as set forth in claim 1 or 2 wherein said aldehyde is t-cinnamaldehyde.

4. A composition as set forth in claim 1 or 2 wherein said aldehyde is t-cinnamaldehyde and said surfactant is an anionic surfactant.

5. A composition as set forth in claim 4 wherein said anionic surfactant is an alkyl aryl sulfonate.

6. A composition as set forth in claim 1 or 2 wherein said aldehyde is t-cinnamaldehyde and said surfactant is a cationic surfactant.

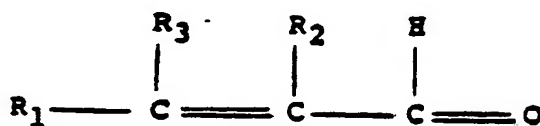
7. A composition as set forth in claim 6 wherein said surfactant is dodecylpyridinium bromide.

8. A composition as set forth in claim 1 or 2 wherein said aldehyde is t-cinnamaldehyde and said surfactant is a nonionic surfactant.

9. A composition as set forth in claim 8 wherein said surfactant is the reaction product of trimethyl-1-heptanol with 7 mols of ethylene oxide.

10. A method for inhibiting the attack of aqueous corrosive fluids on ferrous metal which comprises contacting said ferrous metal with a composition comprising:

(A) an  $\alpha,\beta$ -unsaturated aldehyde having the general formula:



wherein:

R<sub>1</sub> represents a saturated or unsaturated aliphatic hydrocarbon group containing from about 3 to about 12 carbon atoms, a substituted saturated or unsaturated aliphatic hydrocarbon group containing from about 3 to about 12 carbon atoms and also containing one or more non-interfering substituents, an aryl group, a substituted aryl group containing one or more non-interfering substituents, or a non-interfering substituent per se.

R<sub>2</sub> represents hydrogen, a saturated or unsaturated aliphatic hydrocarbon group containing from 1 to about 5 carbon atoms, a substituted saturated or unsaturated aliphatic hydrocarbon group containing from 1 to about 5 carbon atoms and also containing one or more non-interfering substituents, an aryl group, a substituted aryl group containing one or more non-interfering substituents, or a non-interfering substituent per se, and

R<sub>3</sub> represents hydrogen, a saturated or unsaturated aliphatic hydrocarbon group containing from about 3 to about 12 carbon atoms, a substituted saturated or unsaturated aliphatic hydrocarbon group containing from about 3 to about 12 carbon atoms and also containing one or more non-interfering substituents, an aryl group, a substituted aryl group containing one or more non-interfering substituents, or a non-interfering

substituent per se.

with the total number of carbon atoms in substituents represented by  $R_1$ ,  $R_2$  and  $R_3$  ranging from 1 to about 16, and

(B) a surfactant, in particular as defined in claims 4 to 9.

- 5 11. The method for inhibiting the attack of aqueous corrosive fluids on ferrous metal set forth in claim 11, wherein said aldehyde is present in an amount of from about 0.01 to about 4 percent by weight and said surfactant is present in an amount of from about .005 to about 1 percent by weight, said percentages being based on the total weight of said aldehyde, said surfactant and said aqueous corrosive fluid.

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
X	CHEMICAL ABSTRACTS, vol. 105, no. 18, 3rd November 1986, page 516, abstract no. 160812f, Columbus, Ohio, US; F.B. GROWCOCK et al.: "Inhibition of steel corrosion in hydrochloric acid by trans-cinnamaldehyde", & PROC. - ELECTROCHEM. SOC. 1986, 86-7(SURF., INHIB., PASSIVATION), 104-22 * Page 104, paragraph 3; page 105, paragraphs 3,5; page 106, paragraph 1 *	1-11	C 23 F 11/12 C 23 F 11/04 E 21 B 41/02
X	US-A-3 325 410 (H.E. CROTTY) * Claims 1,3,7; column 2, line 19 - column 3, line 52; column 4, lines 7-12 *	1,2	
A,D	US-A-3 589 860 (Z.A. FOROULIS) * Claims 1-9; column 5, lines 10-29 *	1-3,10, 11	
A	US-A-2 571 739 (G.A. MARSH) * Claims 1-8; column 4, table 1; column 5, lines 55-68 *		TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
A	WERKSTOFFE UND KORROSION, vol. 29, 1978, pages 461-468, Verlag Chemie, GmbH, Weinheim, DE; J.D. TALATI et al.: "Aldehydes as corrosion inhibitors for aluminium-manganese alloys in potassium hydroxide"		C 23 F E 21 B
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14-12-1987	Examiner DE ANNA P.L.
CATEGORY OF CITED DOCUMENTS			
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